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Thermal Transformations of Cubane Derivatives

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Abstract—The thermal degradation of the cubane moiety in 1,4-cubanedicarboxylic acid, its dimethyl ester, and 1,4-dibromocubane in a condensed state were studied by calorimetry. The kinetic parameters and the composition of products, as determined by ^{1}H and ^{13}C NMR spectroscopy, are consistent with a biradical reaction mechanism. The presence of carboxyl groups capable of resonance conjugation stabilizes a biradical and increases the rate of isomerization of the acid and ester by a factor of 20, as compared with that of cubane. Bromine as a substituent has almost no effect on the rate of cubane thermolysis. The primary biradical is rapidly isomerized to corresponding cyclooctatetraene derivatives. A detailed reaction scheme is presented, and the relative rates of individual steps of the process are considered.

INTRODUCTION

The intensive development of the synthetic chemistry of cubane derivatives [1, 2] has stimulated the study of their thermal stability. However, these compounds remain poorly investigated, as compared with other types of strained cyclic structures [3]. Published data are restricted to information on the structural isomerization of cubane in a gas phase [4, 5]. This reaction occurs at a detectable rate at temperatures of about 200°C. Among the saturated carbocyclic compounds containing no cyclopropane rings, only compounds like bicycle[2.2.0]hexane are characterized by a higher rate of pyrolysis than that of cubane [3]. The degradation of small rings usually occurs by a biradical mechanism. The main factors responsible for the apparent activation energy of C–C bond opening in a ring are the biradical stabilization energy, which increases in the presence of substituents capable of resonance conjugation, and a decrease in steric hindrances to resonance. For example, substituents such as phenyl, vinyl, and carbonyl groups decrease the activation energy of cyclopropane or cyclobutane degradation by 30 kJ/mol or more. At the same time, halogens as substituents have almost no effect on the rate of cyclobutane decomposition. It is likely that rate changes exhibit an analogous behavior under the action of substituents in the case of cubane, and it is of interest to determine these changes quantitatively. In this work, we studied the isomerization reactions of dimethyl 1,4-cubanedicarboxylate (**1**), 1,4-cubanedicarboxylic acid (**2**), and 1,4-dibromocubane (**3**). In these compounds, substituents are atoms or thermally stable groups, which provide an opportunity to observe the degradation of a cubane fragment and to determine its stability. The reaction was studied using a high-performance calorimetric technique, which allowed us to continuously record reaction kinetics. NMR spectroscopy was used for correcting the calorimetric procedure and analyzing the products.

EXPERIMENTAL

The rate of heat evolution in the course of the conversions of compounds **1**–**3** was determined using a differential microcalorimeter with a sensitivity of 10^{-6} W, which operated in scanning and isothermal modes (Fig. 1). The design of the calorimeter allowed us to combine a comparatively large volume of a metal ampule (1.4 cm^3) with a sufficiently small time constant (~50 s). The time of changing from the scanning mode to the isothermal mode was 5 min. These characteristics allowed us to measure the rates of heat evolution at

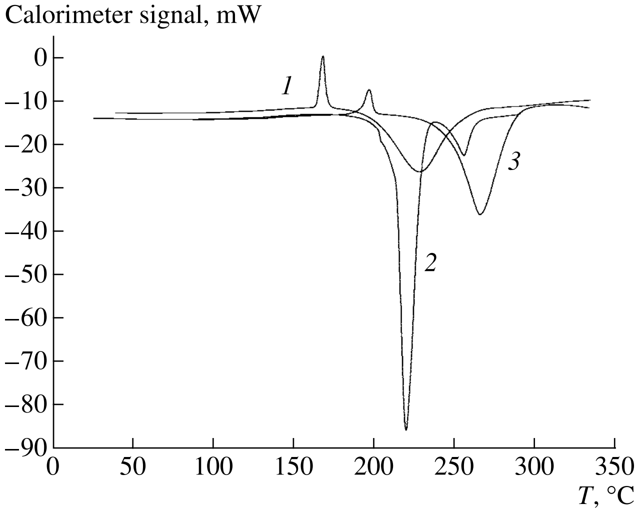


Fig. 1. Rates of heat evolution in the course of the conversion of compounds (*1*) **1**, (*2*) **2**, and (*3*) **3** at a heating rate of 1 K/min.

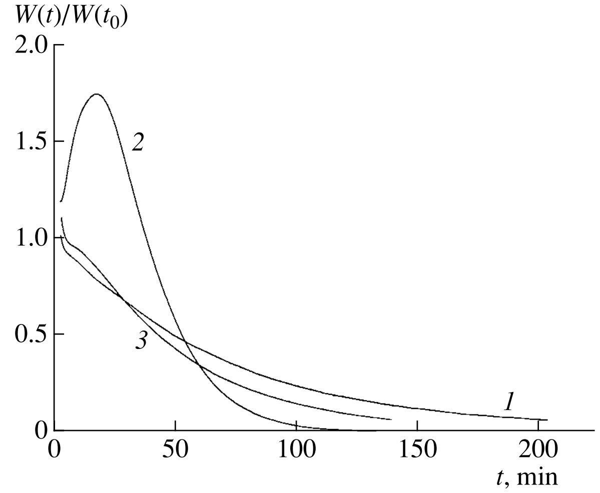


Fig. 2. Relative rate of heat evolution in the conversion of (*1*) **1** at 206.4°C, (*2*) **2** at 203.8°C, and (*3*) **3** at 244.3°C.

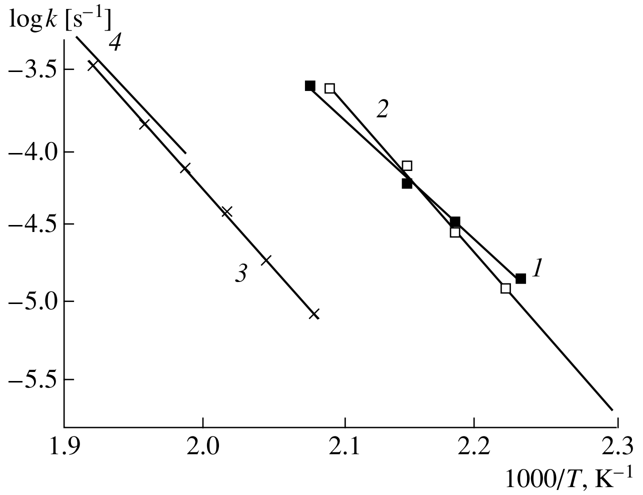


Fig. 3. Arrhenius plots for the rate constants of conversion of (*4*) cubane and compounds (*1*) **1**, (*2*) **2**, and (*3*) **3**.

sample weights of 5–20 mg to a high accuracy, to control rapidly the position of a baseline, and to use efficiently the method of isothermal increments for determining rate constants. The melting points of Ga, In, Sn, and NH_4NO_3 were used for the calibration of the calorimeter. Heat evolution was detected with a TZ 4620 analog recorder using a digital-to-analog converter, and digital signals were written as *.dat files and subsequently treated.

The ^1H and ^{13}C NMR spectra were measured on a Bruker CXP 200 spectrometer. Conversion was estimated by a stopped-reaction method with the use of a number of equal samples (40 mg each in 0.4-cm^3 ampules) for each particular compound. After stopping the reaction, the reactor was rapidly cooled, the ampules were opened, and equal amounts of a solvent (DMSO-d_6 + 20 vol % CCl_4 + 0.5 vol % TMS) were added. The resulting solutions were sealed in standard ampules for NMR measurements. The decrement of the initial substance in the sample was evaluated from a decrease in the integrated intensity of its signals, which was calibrated using the residual proton signal of DMSO-d_6. In all of the NMR experiments, the absence of saturation was obeyed; in this case, it is believed that $\eta = 1 - I_i/I_0$, where I_i and I_0 are the integrated intensities of signals from converted and reference samples, respectively.

RESULTS AND DISCUSSION

Figure 2 shows the shapes of the heat-evolution rate–time curves for all of the three tested substances. The isomerization of ester **1** occurs in a liquid phase in accordance with a first-order rate law, and it is not difficult to calculate the rate constants of this reaction. The conversion of acid **2** occurs in a solid state, and this process is characterized by a topochemical acceleration with time. The rate constants of conversion of compound **2** were calculated from initial rates on the assumption that the heat of reaction remained unchanged in the course of the reaction. The initial portion of curve *3* also exhibited a small increase in the rate of heat evolution; this increase was found to result from the occurrence of consecutive reactions. The higher the temperature, the better the curve is described by a first-order equation; above 225°C, the process was completely limited by the primary step of cubane fragment decomposition.

Table 1 summarizes the kinetic characteristics of the isomerization of compounds **1**–**3**. Figure 3, which shows the temperature dependence of the rate constants of corresponding reactions, clearly illustrates the ratios between the rates of conversion of cubane derivatives. In the isothermal mode, the colorimeter temperature remained constant to within ±0.1 K. The accuracy of temperature and heat-evolution rate measurements was 0.10 and 0.15%, respectively, as checked by the melting of Ga, In, Sn, and Pb. The error in the determination of rate constants in replica experiments was equal to 10–15%. The activation energy was measured to within 4–6 kJ/mol, which corresponds to a change in the preexponential factor by 0.5–0.7 logarithmic units.

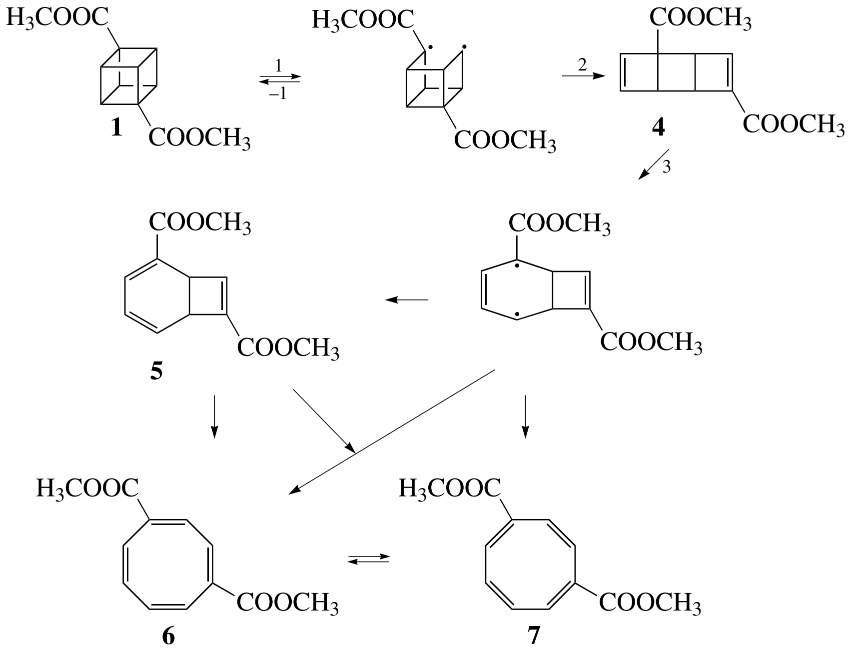
The rate constants of isomerization of compounds **1** and **2** are similar and are higher than the corresponding value for the conversion of unsubstituted cubane in vapor [4] by a factor of 20.

Using NMR spectroscopy, we found that isomeric cyclooctatetraene derivatives (see the scheme) were the only products of thermal reactions with the participation of **1** and **2**. These products undergo slow reactions at temperatures of ~200°C. Long-lived intermediate products were not detected in the conversion of compounds **1** and **2**.

Compounds **6** and **7**, which are shown in the scheme, were identified based on NMR spectra with consideration for published data on related compounds [6] and experimental results obtained using $^{13}C\{^1H\}$DEPT135. The ^1H NMR spectrum of isomer **6** exhibited a singlet from H 7, 8 atoms with $\delta = 6.08$ and two unresolved multiplets with the width at half height $\Delta\nu_{1/2} \cong 5$ Hz from H 3, 4 with $\delta = 6.10$ and from H 2, 5 with $\delta = 6.98$ in the olefin region. The ^{13}C NMR spectrum (with proton decoupling) exhibited singlets from C 3, 4 atoms with $\delta = 130.4$, from C 7, 8 with $\delta = 132.2$, and from C 2, 5 with $\delta = 141.6$. The ^1H NMR spectrum of isomer **7** shows a singlet from H 2, 3 with $\delta = 7.03$ and an unresolved multiplet from H 5, 6, 7, 8 with $\delta = 5.99$ and $\Delta\nu_{1/2} \cong 5$ Hz. The ^{13}C NMR spectrum of this isomer exhibited three singlets from C 6, 7 with $\delta = 129.2$, from C 5, 8 with $\delta = 132.8$, and from C 2, 3 with $\delta = 139.8$. The ^1H NMR spectrum of isomer **6** clearly exhibited an unequal doublet (2 : 1) due to the $COOCH_3$ group with $\delta = 3.80$, whereas the spectrum of **7** exhibited an analogous doublet with $\delta = 3.81$. An analogous NMR spectrum with similar parameters was obtained for compound **2**.

Dibromocubane **3** is much more stable than compounds **1** and **2**. In the temperature region of its isomerization (above 200°C), substituted cyclooctatetraene isomers, which are final products in the case of compounds **1** and **2**, are unstable; they undergo further transformations and thus become intermediate products. It can be seen in Fig. 3 that the intense conversion of **3** began at a higher temperature than that in cyclooctatetraene derivatives formed from compounds **1** and **2**. In the case of **1**, this conversion occurred immediately after the reaction of the parent substance; as a result of this, the peak of this substance broadened. In the case of **2**, the peaks due to the transformation of solid dicarboxy-substituted cyclooctatetraenes and the parent substance are separated from each other, and the peak of the derivative lies at the beginning of the region of transformation of compound **3**. Because of the slow conversion of an intermediate, of the reaction involving **3** at temperatures lower than 220°C changed with time to introduce uncertainty into the determination of the rate constant from the initial portion of the heat-evolution curve. The initial step became the rate-limiting step only from 225°C, and the heat-evolution curve was described, as mentioned above, by a first-order equation. At the edge of the temperature range in which the conversion of **3** was studied (225–240°C), the Arrhenius rate law was obeyed (Fig. 3). It can be seen in Fig. 3 and the table that the introduction of bromine as a substituent into cubane exerted a small stabilizing effect.

Current concepts of the biradical mechanism of small-ring opening [3] allowed us to describe the sequence of steps in the conversion of **1** into final products by the reaction scheme given below.



Scheme. Reaction sequence of product formation in the isomerization of compound **1**.

At the first step, a C–C bond adjacent to a substituent in compound **1** is broken to form a biradical. The activation energy of this endothermic process is $E_1 = \varepsilon_0 + \Delta H_1$, where ε_0 is the energy barrier, and ΔH_1 is the

Kinetic characteristics of the isomerization of compounds **1–3**

Compound	Phase state	ΔQ, kJ/mol	T, °C	k, s^{-1}	E, kJ/mol	$\log A\,[s^{-1}]$	Rate constant at 200°C, s^{-1}
Cubane [4]	Gas		230–260		180	14.68	5.9×10^{-6}
1	Melt	430	175.4	1.4×10^{-5}	156	13.27	1.2×10^{-4}
			185.0	3.3×10^{-5}			
			192.4	5.7×10^{-5}			
			208.1	2.4×10^{-4}			
2	Solid phase	290	177.5	1.2×10^{-5}	195	17.68	1.4×10^{-4}
			185.2	2.8×10^{-5}			
			192.5	7.3×10^{-5}			
			204.8	2.3×10^{-4}			
3	Melt	450	207.6	8.3×10^{-6}	192	15.74	3.8×10^{-5}
			215.7	1.8×10^{-5}			
			222.5	3.8×10^{-5}			
			230.0	7.2×10^{-5}			
			237.5	1.4×10^{-4}			
			247.4	3.3×10^{-4}			

heat of the reaction. The conjugation of free electrons in the biradical with the carboxyl group increases the stabilization energy of the biradical, as compared with that of unsubstituted cubane. This results in a decrease in ΔH_1 and, likely, in an increase in ε_0. In general, the value of E_1 decreases. The experimentally found activation energy of conversion of compound **1** (which was determined to within 4 kJ/mol) is lower than that of cubane by 20 kJ/mol. With consideration for difference between the statistical factors in the isomerization relations of **1** and cubane (6 and 12, respectively), the preexponential factor in the Arrhenius equation that describes the conversion of **1** was found to be smaller than that in the case of unsubstituted cubane by a factor of 5. This is due to the impossibility of the hindered internal rotation of the carboxyl group in the activated complex. An analogous effect of a decrease in preexponential factors was observed in the degradation of phenylcyclopropane and acetylcyclobutane [3].

The second step of the reaction is the isomerization of the cubane biradical and its derivatives into diene **4**, which occurs readily because the free electrons in the biradical are arranged in parallel to the π electrons of the broken C–C bond. Thus, it is believed that $k_2 > k_{-1}$. In turn, diene **4** also undergoes isomerization by a biradical mechanism. This isomerization occurs either directly or, very likely, through the step of the formation of 2,7-R_2-bicyclo[4.2.0]octatetraene (**5**) to form 1,6- and 1,4-cyclooctatetraene derivatives **6** and **7**. In this case, $k_3 \gg k_1$. This conclusion is consistent with the well-known fact that the rates of degradation and isomerization of unsaturated rings are much higher than the rates of conversion of saturated ring systems [3]. Cyclooctatetraene derivatives **6** and **7** are always formed (from both **1** and **2**) in a 2 : 1 ratio, which corresponds to the establishment of an equilibrium between these isomers even at room temperature [6].

It is believed that the conversion of dibromide **3** is described by an analogous reaction scheme. As mentioned above, the difference between compounds **1** and **2**, on the one hand, and compound **3**, on the other hand, is that cyclooctatetraene derivatives, which are the final products of the reactions involving **1** and **2**, also undergo transformations because of a higher reaction temperature in the case of compound **3**. In this case, they act as intermediate products.

Thus, we found that the introduction of the carboxyl group increased the rate of reaction by a factor of 20, whereas bromine as a substituent had only a small stabilizing effect. Qualitatively, these results are consistent with published data for cyclobutane [3]. At 380°C, when the rate constant of cyclobutane degradation is 6×10^{-6} s^{-1} (i.e., is equal to the rate constant of cubane decomposition at 200°C), the acetyl group increased the rate of reaction by a factor of 35, whereas fluorine and chlorine noticeably stabilized the ring. The degradation of the cubane fragment in cubane derivatives obeys laws that are also typical of other strained ring systems. The difference can only be quantitative; it can manifest itself in the effects of substituents. These effects can be evaluated by studying specially selected series of compounds with identical substituents.

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